### Comments from Professor David L. Sedlak, University of California, Berkeley

### Overarching Questions:

- 1. Are data used in the report reliable and appropriate, and is the treatment of the data defensible?
- 2. Does the report as a whole support its scientific conclusions and recommendations?
- 3. Does the analysis present a sufficiently compelling scientific justification to proceed with the TMDL adoption and implementation plan as proposed?
- The development of a TMDL for mercury in San Francisco Bay is very challenging and I believe that the authors of the report should be commended for their efforts. In my opinion, the report articulates the state of the science with respect to mercury in San Francisco Bay and the various approaches that can be used to ameliorate the risks that mercury poses to humans and wildlife. The authors have done a good job identifying uncertainties in the data and designing a TMDL that can be adapted as additional information becomes available. Although certain elements of the report could be improved, I believe that the plan should be adopted in a timely manner. The report makes it clear that mercury really is a problem in San Francisco Bay and that a modest allocation of resources can help solve the problem.

# Have we reasonably described the nature of the water quality problem of mercury in San Francisco Bay?

The problem statement identifies threats to human health and endangered species as the main reasons for addressing mercury contamination in San Francisco Bay. The problem statement is clear and concise. However, given the importance of these points in establishing everything else that follows, it may be appropriate to include a few additional details in the text as opposed to referencing scientific papers (several of which would be difficult for the readers to access). Specifically, it might be helpful to include data on Hg concentrations in California Clapper Rail eggs.

#### Minor comments related to chapter 2:

- Page 4, first sentence: "Mercury is a persistent...metal that does not degrade...". I agree that this is a relevant issue, but mercury is persistent because it is a metal (with the exception of nuclear decay, metals don't degrade).
- Page 7 and elsewhere in document: the unpublished reference, Wiener *et al.* is cited repeatedly. From the citation it appears to be a book chapter summarizing findings of other studies. Therefore, it probably makes more sense to cite the primary references, which I presume already are published.
- Page 7, "Because of the small foraging range...its eggs are particularly vulnerable to local methylmercury levels." I think it makes more sense to say something like, "its eggs

- are affected by elevated methylmercury concentrations to a greater degree than other local bird species."
  - a) Have we clearly described the steady-state box model employed in the analysis?
  - b) Have we reasonably supported our rationale for employing a steady-state box model for the purpose of the mercury TMDL analysis?
- I found Figure 3.1 and the related discussion to be somewhat confusing with respect to the issue of sediment erosion. It was not until I finished reading the report that I understood the actual approach that was used. The box model defines both the water column and the active sediment layer as being part of the box used in the mass balance calculation. I suppose that this means that the shaded area at the bottom of the figure, with the up arrow, represents the sediment beneath the active layer. However, from the drawing it seems to be included in the box. Moreover, it was unclear initially that the term net erosion refers to the fact that bed erosion is greater than the rate of sediment burial. This approach contrasts with the approach taken for air/water exchange of mercury in which deposition and evaporation are indicated explicitly. The assumption that there is a net loss of contaminated sediment from the bed sediments is critical because it accounts for most of the long-term improvement in water quality projected by the study's authors. It may be appropriate to discuss this in more detail in this first section on the box model.

Minor issues in chapter 3:

- Page 12, paragraph 2, last sentence: I believe the word "is" should be placed before "adequate".
- Page 13, figure 3.1: The sources in the arrow on the left hand side of the figure only contain a partial list of the sources considered (*e.g.*, municipal and industrial wastewater are not included). Either these other (minor) sources should be included or a note should be added to the figure indicating that it's a partial list.
- Page 13, Figure 3.1: Technically speaking, only the top 15 cm of dredged sediments represent a loss from the box considered in the model. The remaining sediments could enter the box later, but only if they are in the area of the bay where net sediment loss occurs. I think this point might be addressed in chapter 4 as well.
  - a) Are the source categories clearly defined?
  - b) Are the source estimates and estimation methodologies clearly stated for each source category?
  - c) In view of the data available, are the estimation methods employed reasonable and scientifically sound?

- My biggest concern with the scientific approach used to derive mercury loads is the implicit assumption that mercury concentrations are equal in suspended and settled sediments and that mercury concentrations in suspended sediments are not affected by the source of the TSS. Throughout the report, sediment mercury concentrations are calculated from water column mercury measurements by subtracting filtered Hg concentrations from total Hg concentrations that then are divided by TSS. This approach gives the mercury concentration in suspended sediment and not necessarily the concentration of mercury in Bay sediments. This is especially true if the suspended sediments contain a higher proportion of fines relative to sand sized particles. I suspect that this approach will overestimate mercury concentrations from these sources, which is a conservative approach. However, it could cause a problem when mercury concentrations calculated by this method are compared with data calculated by direct sampling of sediment.
- I found the explanation of sources as summarized in Table 4.1 to be rather confusing. For example, the report states that the Central Valley mercury load is 440 kg/yr and proceeds to use this to estimate the mercury concentration in the Central Valley sediment (0.26 ppm). The method used by the SFEI to estimate the mercury flux is unclear, and it appears to use water column mercury measurements extrapolated at X2. The SFEI document was not readily available to me and I found it difficult evaluate the scientific basis of the estimate from the information provided.
- The statement associated with the first bullet on page 21, indicates that mean values will be more useful than median values for assessing loads. However, stormwater may be a special situation because the overall flow (an hence the overall contribution to the annual mass loading from any one data point) will vary with the size of the storm event. In this case, the best approach probably is a volume-weighted mean as opposed to either a mean or a median value.
- Page 24: In the section on the stormwater sediment load the calculated mass of sediments (8.5 M kg/yr) is obtained by subtracting the urban sediment load (36 M kg/yr) from the total sediment load (44 M kg/yr). I presume that the apparent discrepancy is due to a rounding error or by a failure to show the data to the appropriate number of significant figures.
- Page 30, Table 4.7: The authors may want to review the data in Table 4.7. I believe that the UC Berkeley and Stege Marsh sites have been partially or completely remediated during the past year.

## a) Are the target derivations clearly stated and adequately supported by available information?

The fish tissue target on page 34 is somewhat ambiguous. The report states (p. 33), "Therefore, 0.2 ppm mercury in fish tissue is proposed as a target to protect human health." The figure showing fish tissue concentrations (Figure 5.1) depicts median concentrations whereas the text (p. 34) sates, "...the fish tissue target applies to the

- average mercury concentration in a collection of fish..." This is a minor point, but one that can be clarified easily.
- The sediment target refers to "sediment mercury concentrations" as particle bound mercury mass divided by sediment mass. As indicated in a previous comment, this may not equate directly to the concentration of mercury in bay sediment. To avoid confusion, I suggest that the authors employ a more specific term here and throughout the document and basin plan revision (*e.g.*, suspended sediment mercury concentrations).
- Page 36: The authors suggest that the median is more appropriate as a descriptor of the data because the concentration data "appear to be log-normally distributed". If the data exhibit a log-normal distribution I believe that the mean of the log-transformed data may be a better descriptor if the goal is to assess the average dose received by an individual who regularly consumes fish from San Francisco Bay. If the authors want to say that the data follow a log-normal distribution, a statistical test should be used to prove the assertion. I believe that for the purpose of this study, the median will suffice, too.
- Page 38, The last paragraph states that, "22% of the estimated sediment mercury concentrations during the four-day period exceed 0.025 µg/L....but actual exceedances of the Basin Plan Objective are unlikely." The data in Figure 5.3 suggest that there will be numerous periods in a year in which the 4-day target will be exceeded. I think the point here is that the 0.025 µg/L standard for total Hg is inappropriate for a basin in which TSS values above 100 mg/L frequently occur. I know that the authors may not have a legal basis for disagreeing with the standard, but the data suggest that the new targets still will lead to periods in which the 4-day target for total Hg is exceeded.
- 9 Figure 5.3: The x-axis label on the figure ("minutes after 3/16/97 17:45") should be changed to something that is more easily understood by the reader.
- There is no clear point of compliance in this TMDL. San Francisco Bay is very large and it's hard to see how we will be able to monitor the progress towards compliance with these objectives. The approach chosen by the authors is to compare results to averaged data from the RMP. It may be more appropriate (form a scientific standpoint) to subdivide the basin and compare within different regions (e.g., north bay vs south bay). For example, samples collected exclusively from the South Bay might indicate higher concentrations of mercury due to the abandoned mining facility and associated sediments in Coyote Creek. If there is a localized problem it may not be appropriate to average all of the data for the bay. I suggest that the authors get involved in the details of the samples that will be used to assess fish, bird egg and sediment mercury concentrations (e.g., how many samples will be collected, where should they be collected, at what frequency, what time of year). This may require a workshop with the RMP and the stakeholders, but it seems that the basis for assessing progress should be established and efforts should be made to compare data from similar samples over the next 20 years.

- a) Are the linkages between sources and the numeric targets clearly stated and scientifically sound?
- b) Have we presented a plausible argument that reducing sources of mercury will result in attainment of proposed targets?
- c) There are several key assumptions put forth in this section to complete the linkage between mercury loads and fish tissue mercury concentrations. In light of available data, are these assumptions reasonable?
- On page 43 the authors state, "Mercury methylation rates in surface sediment directly relate to mercury concentrations in the sediment." At first, this appears to be inconsistent with the statements in the first paragraph on page 43 about how environmental variables affect methylation rates. I think that this sentence should be clarified by stating that in a given location, methylmercury production is probably proportional to total mercury concentrations.
- Page 41: The sediment-to-water partition coefficient is usually defined as  $K_d$  or  $K_D$ . I am unfamiliar with the notation  $K_{db}$  used here. Is this a typographical error?
- Page 41, mercury sources and sediment: It is true that most of the mercury in San Francisco Bay is associated with sediment, but this is due to the relatively high suspended sediment load as much as it is due to the high affinity of sediments for particles. If the average TSS in SF Bay were closer to 10 mg/L it would not be appropriate to ignore the filterable mercury. This paragraph could be improved by addition of a simple calculation: "Using this K<sub>d</sub> value and a typical TSS for San Francisco Bay of 100 mg/L, approximately \_\_\_\_\_ % of the mercury would be associated with particles at equilibrium."
- Page 42, the last sentence on the page on the detection of methylmercury in the Bay seems to be out of place. I suggest adding a short paragraph summarizing the typical methylmercury concentrations detected in SF Bay and how it compares to total Hg concentrations.
- Page 44: last paragraph: I suggest editing the first and second sentences here. Change "get" to "obtain" and "multitudes" to "numerous".
  - a) Are the load allocations and calculation methodologies clearly stated for each source category?
  - b) Are the calculation methodologies for arriving at categorical load allocations reasonable?
  - c) When load allocations are further distributed among contributing entities (e.g. wastewater and urban stormwater), is the methodology for distributing the load allocation clearly stated and reasonable?
  - d) Given the scarcity of information concerning relative bioavailability and the degree to which mercury from different sources undergoes methylation, is it reasonable for us to assume that all mercury sources are equally bioavailable?

- e) There is a discussion in this section regarding the response time of sediment concentrations that makes use of a box model to generate an estimated response time on the order of 100 years. Based on the available information, is this areasonable conclusion about physical constraints on the expected response time of mercury concentrations in sediments?
- The load allocations do not contain a term to allow for future growth, as often is done in TMDLs. One potential implication of this approach is that it could place caps on the volume of effluent discharged by wastewater treatment plants. Because the allocation for wastewater treatment plants is based upon current discharges, a treatment plant in a rapidly growing area might have to engage in water recycling or install advanced wastewater treatment processes to comply with this TMDL. Although water recycling and advanced treatment are reasonable objectives, I am not sure that it would be appropriate to require such measures as part of this particular TMDL program. Although the volume of wastewater discharged by the sum of all of the dischargers may not be increasing rapidly, I suggest that the authors address the issue of future increases in wastewater effluent flow in more detail.
- The study from Conaway *et al.* (2003) implies that wastewater effluent could be an important source of methylmercury to the estuary (p. 47). To further complicate the picture, the authors may want to consider the fact that mercury in municipal wastewater effluent tends to be present as extremely strong complexes, which probably are less amenable to methylation (Hsu and Sedlak, ES&T, 2003, 37, 2743-2749). The paper by Conaway *et al.* (2003) speculates that the increase in methylmercury could be attributable to the labile carbon in the effluent rather than the mercury itself. I believe that any attempt to control the labile carbon in wastewater effluent would be quite complicated and would open up questions about many other sources of nutrients and carbon to the bay.
- Figure 7.2: This figure is very helpful for understanding the effect of the allocations on mercury concentrations. I have a few suggestions that might help to improve the figure: First, not all of your readers will have a color copy of the report. As a result all three lines look very similar. I suggest that at a minimum you use a dotted line for the sediment target. Second, it would help if you could include in the narrative a statement mentioning that the shape of the profiles changes after 100 years when the mercury-contaminated sediments are finally eroded from the bed.
  - a) Have we adequately identified the limitations of the technical information available to us?
  - b) Is the method of ensuring an implicit margin of safety clearly stated and reasonable?
- The limitations in the available technical information and the implicit margin of safety are both explained clearly.

- Page 56: In the section titled, "Margin of Safety" the word "used" should be inserted between "is" and "to" in the second sentence.
- On page 59, in the section titled "Key Points" I believe that the statement that, "reaching the target of 0.2 ppm after at least 120 years" should be reworded to state that the target will be reached "after approximately 120 years".
  - a) Are the actions described in this section reasonable in light of available data?
  - b) Is the adaptive approach to implementation adequately explained and reasonable?
  - c) Is the proposed monitoring program adequate to evaluate progress toward achieving the sediment, fish tissue, and bird egg targets?
  - d) Have we clearly stated the key management questions?
  - e) Have we stated a reasonable approach and schedule for addressing each of the questions?
- The proposed implementation plan for urban stormwater may be considered excessive by the stakeholders. Examples are indicated below.
- Objective (ii) indicates that the stormwater agencies should develop and implement a mercury source control program. In the preceeding text, it is stated, "Urban runoff management agencies can prevent enrichment through various source control and pollution prevention activities, including fluorescent light bulb, electrical switch and thermometer collection and disposal programs, and other household waste collection programs. In many communities, such programs are coordinated by staff of the wastewater treatment plants. At the least, this objective might be viewed as a joint activity with credit awarded to the wastewater treatment plants and stormwater agencies as appropriate.
- The implementation plan also indicates that the stormwater agencies will be involved with development and implementation of monitoring programs. Given the logistical difficulties associated with sampling and analysis of mercury this may not be practical for smaller municipalities.
- Objective (iv) states that the stormwater agencies should, "Conduct studies aimed at better understanding of mercury fate, transport and biological uptake in San Francisco Bay and tidal areas". This broad objective seems to be beyond the scope of an implementation plan for stormwater utilities. Is the implication here that the stormwater agencies should continue to provide funding to the SFEI for monitoring and research activities? A similar comment applies to the statement made on page 69 and 70 that the wastewater and industrial dischargers should, "Conduct studies to better understand mercury fate, transport and biological uptake in San Francisco Bay and tidal areas."

- The section on atmospheric deposition references priorities for the adaptive management plan. It would be appropriate to reference the page of the report where these issues are discussed in more detail (p. 82 in the current draft).
- On page 69, wastewater effluent concentrations are specified that will trigger further investigations. Different values are set for plants equipped with secondary and advanced treatment systems. In my opinion, the term "advanced treatment" should be defined in a more rigorous manner. Do nitrification or effluent filtration count as advanced treatment? While it is likely that effluent filtration will reduce mercury concentrations through the removal of particles, I am not certain that nitrification will result in a reduction in mercury concentrations. Also, these effluent limits seem to be in conflict with the California Toxics Rule (CTR). Does this issue need to be discussed?
- In the section on industrial discharges (p. 70) a mass limit is set for the Bay area refineries. Although I am unfamiliar with operating procedures at the refineries, I recall reading about a controversy surrounding the RWQCB's regulation of dioxin in the refinery effluent in which one of the refineries noted that they were being penalized for dioxin in the rainwater that falls on the refinery. For consistency with the approaches taken for other uncontrollable background sources, I believe that it might be appropriate to account for the mass loading of mercury in rainwater falling on the refinery sites.
- 40 Page 73, third paragraph: delete "of the site" after "site-specific features".
- Some of the research referred to in the section titled, "competitive process control" has been published and should be referenced instead of the current unpublished personal communication. The citation is: Mehrotra A.S., Horne A.J. and Sedlak D.L. (2003) Inhibition of net mercury methylation by iron in *Desulfobulbus propionicus* cultures: implications for engineered wetlands. *Environ. Sci. Technol.* 37, 3018-3023.
- Another important variable to be considered in the prevention of mercury methylation is salinity. Available data suggests that methylation rates are highest in brackish waters of intermediate salinity and this could influence the selection of sites for restoration.
- The section on adaptive management poses the question, "how should monitoring efforts be modified to improve our ability to detect trends?" There appears to be a lack of coordination between the TMDL's authors and the scientists responsible for coordinating the monitoring programs. For example, on page 78 and 79 it is stated that the fish and bird egg sampling will be performed every three years while on page 76 a five-year schedule for evaluation is proposed. This means that the most recent data will be collected at different points in the evaluation cycle. Wouldn't it be more relevant for the adaptive management plan to collect more samples on a five-year cycle, designed to provide new data at the start of the assessment process?
- The fish tissue target concentrations are based upon fish caught on sampling cruises. It might be more cost effective and provide a better representation of the doses received by consumers if the fish tissues were collected at the docks and boat ramps where sport

- fisherman congregate. At the least, it would be worthwhile for risk assessment to know the average sizes and mix of species consumed by local fisherman.
- On page 79, the authors state that the data will be transformed until they obtain a "reasonably normal distribution". This term should be specified in more detail by using a statistical test for normalcy with a specific alpha value for rejecting the null hypothesis. I am not an expert in statistics, but I suspect that these issues could make a difference when comparing data to a 99% confidence interval.
- The target for sediment compares the results to the median concentration for all sites determined by the RMP and the fish target is compared to an average value derived from a regression equation. These approaches contrast with the bird egg target, which will be established by comparing results to a 99 th percentile for a mixture of different species of birds. I do not have any information on the distribution of trace element concentrations in bird eggs, but I suspect that there may be a broad range of concentrations detected in individual eggs and a 99th percentile value of less than 0.5 ppm might be difficult to achieve. Prior to using a 99th percentile, the RWQCB should review available data on mercury distributions in bird eggs at various sites. In addition, the selection of a 99th percentile value should be discussed in terms of its consistency with other regulations designed to protect wildlife.
- Another unknown related to the approach that may be appropriate to address with further research is related to the residence time of sediments and water from different sources. It is likely that sediments from the Central Valley that are deposited during rain and runoff events are more likely to pass directly through the Golden Gate then discharges to the South Bay. This may give additional motivation to addressing sources such as the Guadalupe River.
- On page 86, the target mercury concentrations are specified as 0.2 ppm for sediments and fish and "less than 0.5 ppm" for bird eggs. I believe that the authors should either state that the current target is 0.5 ppm or should be more specific about the target.
- Page 87, change top as follows: "the sediment mercury concentrations are expected to decline from 0.44 ppm..."
- Page 96: It is stated, "the Bay Area currently spends roughly \$45 million..." I presume that this is an annual cost. If so, it should be stated.
- Some of the economic costs associated with the TMDL are not known with much certainty (pages 95-99). Given the long-term nature of the program and the adaptive management framework, it may be appropriate to include the collection of more data on costs and benefits as part of the adaptive management framework.